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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US90/01703 <b>(22) International Filing Date:</b> 2 April 1990 (02.04.90)  <b>(30) Priority data:</b> 340,182                      19 April 1989 (19.04.89)                      US  <b>(71) Applicant:</b> GAF CHEMICALS CORPORATION [US/ US]; 1361 Alps Road, Wayne, NJ 07470 (US).  <b>(72) Inventors:</b> TAZI, Mohammed ; 33 Claremont Terrace, Wayne, NJ 07470 (US). HARWOOD, Harold, J. ; 1692 Mohican Road, Stow, OH 44224 (US).  <b>(74) Agents:</b> MAUE, Marilyn, J. et al.; GAF Corporation, Pa- tent Dept., Building No. 10, 1361 Alps Road, Wayne, NJ 07470 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European + patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (Eu- ropean patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European pa- tent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR PRODUCTION OF COPOLYMERS OF MALEIC ANHYDRIDE AND AN ALKYL VINYL ETHER IN A STERICALLY HINDERED MONOETHER SOLVENT  <b>(57) Abstract</b>  What is described herein is a process for making copolymers of maleic anhydride and a C <sub>1</sub> -C <sub>8</sub> alkyl vinyl ether. In this process, a reactor is precharged with a solution of maleic anhydride in a sterically hindered monoether solvent and the alkyl vinyl ether monomer is fed thereto. Copolymerization is effected in the presence of a free radical initiator. A pumpable slurry of the copolymer in the reaction medium is formed upon polymerization, from which a copolymer product which is substantially a benzene-free powder is obtained.		

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- 1 -

PROCESS FOR PRODUCTION OF COPOLYMERS OF  
MALEIC ANHYDRIDE AND AN ALKYL VINYL ETHER  
IN A STERICALLY HINDERED MONOETHER SOLVENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for producing a copolymer of maleic anhydride and a C<sub>1</sub>-C<sub>8</sub> alkyl vinyl ether monomers, and, more particularly, to slurry polymerization of such monomers in a sterically hindered monoether solvent in the presence of a free radical initiator.

2. Description of the Prior Art

Copolymers of maleic anhydride and alkyl vinyl ethers are conveniently prepared by free radical precipitation polymerization of the monomer mixture in an aromatic hydrocarbon solvent, e.g., benzene, in the presence of a dispersion aid, such as a protective colloid. However, isolation of the copolymer as a powder requires an expensive process step, and it is difficult to remove the toxic aromatic hydrocarbon solvent from the copolymer.

Accordingly, it is an object of the present invention to provide an improved process for the production of copolymers of maleic anhydride and a C<sub>1</sub>-C<sub>8</sub> alkyl vinyl ether in the presence of a free radical polymerization initiator.

- 2 -

Another object of the invention is to prepare such copolymers by free radical slurry polymerization of the monomer solvent, wherein the copolymer is formed as a slurry in the reaction medium, and from which copolymer powders which are substantially benzene-free and which have low specific viscosities can be obtained easily.

A feature of the present invention is the use of a sterically hindered monoether as the reaction solvent in the process of slurry polymerization of monomers of maleic anhydride and an alkyl vinyl ether.

Another feature herein is the provision of copolymer powders of maleic anhydride and an alkyl vinyl ether which have a specific viscosity of less than about 2.1, and contain less than about 0.1% residual solvent, and is benzene-free.

These and other objects and features of the invention will be made apparent from the following more particular description of the invention.

#### SUMMARY OF THE INVENTION

An improved process for making copolymers of maleic anhydride and a  $C_1-C_8$  alkyl vinyl ether is described herein. The process comprises precharging a reactor with a solution of maleic anhydride in a sterically hindered monoether and feeding a  $C_1-C_8$  alkyl vinyl ether thereto. Slurry polymerization is effected in the presence of a free radical initiator. The copolymer is formed as a pumpable slurry in the reaction medium. Powders of the copolymer can be obtained by discharging the slurry from the reactor and drying, or filtering and drying. The copolymer powder is characterized by being substantially solvent-free and having specific viscosities

- 3 -

of less than about 2.1. The powder also is benzene-free which contrasts to other solvents used in slurry polymerization, such as benzene, toluene and xylene, which leaves benzene solvent in the product.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, the maleic anhydride monomer reactant is precharged into a reactor as a solution in a monoether solvent which is sterically hindered so that substantially no peroxides can form in the reaction medium. Preferably, this solvent is a saturated, acyclic dialkyl monoether which is sterically hindered with a tertiary butyl group. The remaining group in the molecule can be any  $C_1$ - $C_8$  alkyl radical. The monoether solvent may be further characterized by being benzene-free, of low toxicity, and having a low boiling point.

Suitable monoether compounds include methyl t-butyl monoether.

Typically, the maleic anhydride solution comprises about 1 part by weight maleic anhydride to about 7 parts by weight of the solvent.

The alkyl vinyl ether monomer is fed into the precharged maleic anhydride monomer solution to provide substantially a 1:1 molar ratio of monomers in the reaction mixture. A small excess of the alkyl vinyl ether monomer e.g., about a 10% molar excess or less of the alkyl vinyl ether monomer may be used.

The reaction mixture comprises about 20% by weight monomer solids, or lower, in the monoether solvent.

Suitable alkyl vinyl ethers which are employed for copolymerization with maleic anhydride are  $C_1$ - $C_8$  alkyl vinyl ethers, preferably  $C_1$ - $C_8$  alkyl vinyl ethers, e.g., methyl vinyl ethers, ethyl vinyl ether, n-butyl vinyl ether and vinyl 2-ethylhexyl ether.

- 4 -

The copolymerization is effected in the presence of a conventional free radical initiator. Examples of suitable initiators include peroxy esters, e.g., t-butylperoxy pivalate; diacyl peroxides, e.g., dibenzoyl peroxides, peroxydicarbonates, e.g., bis (4-t-butylcyclohexyl) peroxy dicarbonate; alkyl per esters, dialkyl peroxides, and azonitriles, e.g., azo bis-isobutyronitrile.

The initiator is employed in an amount of about 0.1 to 5% by weight of the monomers, preferably about 0.2 to 2% by weight.

The sterically hindered monoether compound used herein is a solvent for both monomer reactants but only a swelling agent for the copolymer. Accordingly, the polymerization process of the invention produces the desired copolymer product as a slurry in the reaction product mixture which can be easily discharged from the reactor and pumped to a suitable dryer where the solvent and excess alkyl vinyl ether can be removed to provide the copolymer in powder form. Alternately, the slurry can be discharged, filtered, and then dried to provide the copolymer powder.

The polymerization temperature can vary over a wide range but is generally from about 50° to 90°C., preferably from 60° to 70°C.

The copolymerization is preferably carried out under atmospheric pressure or at the pressure of the reactants, and under an inert atmosphere such as is provided by nitrogen gas.

The invention will be illustrated hereinafter by the following examples.

- 5 -

EXAMPLE 1

A reaction mixture at a 20% solids level is prepared by:

Precharging 73.5 g. of MA into 480 g. of methyl t-butyl ether;  
Purging with nitrogen;  
Heating the precharge to 60° C.;  
Adding 0.55 g. of t-butylperoxy pivalate (0.75% by wt. based on MA); and  
Feeding 62 ml. (47.9 g.) of MVE (10% molar excess) over 4 hrs. continuously.

The reaction mixture then is held for 1 hr. at the reaction temperature, cooled to room temperature, and the reaction product slurry is discharged from the reactor. Upon filtering and drying there is obtained a fine, white powder of the copolymer having a specific viscosity of 0.36 (as a 1% solution in 2-butanone).

EXAMPLE 2

The process of Example 1 was repeated at a reaction temperature of 65°C. The specific viscosity of the copolymer product obtained was 0.23.

EXAMPLE 3

The process of Example 1 was repeated using 1.25% by wt. of the initiator at a reaction temperature of 65°C. A copolymer having a specific viscosity of 0.13 was obtained.

- 6 -

EXAMPLE 4

The processes of Examples 1-3 are repeated using di-t-butyl monoether, ethyl t-butyl monoether, and with similar results.

While the invention has been described with reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art. Accordingly, it is intended to be bound by the appended claims only, in which:



- 7 -

WHAT IS CLAIMED IS:

1. A process for making copolymers of maleic anhydride and a C<sub>1</sub>-C<sub>8</sub> alkyl vinyl ether which comprises precharging a reactor with a solution of maleic anhydride in a monoether solvent which is sterically hindered towards formation of peroxides, feeding a C<sub>1</sub>-C<sub>8</sub> alkyl vinyl ether thereto, and polymerizing the reaction mixture in the presence of a free radical initiator to form a slurry of the copolymer product.
2. A process according to Claim 1 wherein said dialkyl monoether is a dialkyl monoether which contains at least one tertiary butyl group.
3. A process according to Claim 1 wherein said monoether is a saturated, acyclic monoether.
4. A process according to Claim 1 wherein said monoether is methyl t-butylether.
5. A process according to Claim 1 wherein said alkyl vinyl ether is present in a molar amount of about 10% or less with respect to said maleic anhydride.
6. A process according to Claim 1 wherein said slurry is discharged from the reactor and the copolymer product is recovered in powder form therefrom.
7. A process according to Claim 1 wherein said alkyl vinyl ether is methyl vinyl ether.

- 8 -

8. A process according to Claim 6 wherein said slurry is discharged, solvent and excess alkyl vinyl ether removed, and the copolymer product obtained in powder form.

9. A process according to Claim 6 wherein said slurry is discharged, filtered and dried to provide said copolymer as a powder.

10. A process according to Claim 6 wherein the copolymer product has a specific viscosity of less than 2 and contains less than 0.5% solvent therein.

11. A copolymer of maleic anhydride and a  $C_1-C_8$  alkyl vinyl ether which is a powder having a specific viscosity of 2.1 or less and a solvent level of 0.2 or less.

12. A copolymer according to Claim 11 wherein said alkyl vinyl ether is methyl vinyl ether.

13. A copolymer according to Claim 11 which is benzene-free.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/01703

<b>I. CLASSIFICATION F SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL.(5): C08F, 34/02, 2/12; U.S. CL.: 526/271,209														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched <sup>7</sup></div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">U.S. CL.</td> <td style="padding: 5px;">526/271, 209</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	U.S. CL.	526/271, 209								
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>*</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">           Date of the Actual Completion of the International Search   <div style="text-align: center; font-weight: bold;">03 MAY 1990</div> </td> <td style="width: 50%; padding: 5px;">           Date of Mailing of this International Search Report   <div style="text-align: center; font-weight: bold;">16 AUG 1990</div> </td> </tr> <tr> <td style="padding: 5px;">           International Searching Authority   <div style="text-align: center;">ISA/US</div> </td> <td style="padding: 5px;">           Signature of Authorized Officer  <div style="text-align: center;">              ALEX H. WALKER           </div> </td> </tr> </table>			Date of the Actual Completion of the International Search  <div style="text-align: center; font-weight: bold;">03 MAY 1990</div>	Date of Mailing of this International Search Report  <div style="text-align: center; font-weight: bold;">16 AUG 1990</div>	International Searching Authority  <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;">              ALEX H. WALKER           </div>								
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